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DECLARATION

I, Hiromi Hase of c/o SHIGA INTERNATIONAL PATENT OFFICE, 2-3-1 Yaesu, Chuo-ku, Tokyo 104-8453 JAPAN, understand both English and Japanese, am the translator of the English document attached, and do hereby declare and state that the attached English document contains an accurate translation of the official certified copy of Japanese Patent Application No. 2003-186941 and that all statements made herein are true to the best of my knowledge.

Declared in Tokyo, Japan

This 1st day of December, 2006

Hiromi Hase

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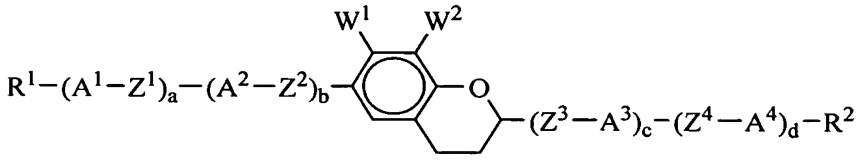
Patent Application No. 2003-186941 filed June 30, 2003

[Document Type] Specification
[Document Title] CHROMAN DERIVATIVE AND LIQUID CRYSTAL COMPOSITION CONTAINING THE SAME
[Claims]

[Claim 1]

A compound represented by general formula (1):

[Chemical Formula 1]



$$R^1-(A^1-Z^1)_a-(A^2-Z^2)_b-\text{(ring with } W^1, W^2, O\text{)}-(Z^3-A^3)_c-(Z^4-A^4)_d-R^2 \qquad (1)$$

(wherein

R^1 and R^2 each independently represents hydrogen, an alkyl group having 1 to 12 carbon atoms or an alkenyl group having 2 to 12 carbon atoms, in which one CH_2 group or at least two CH_2 groups that are not adjacent to each other may be substituted by oxygen or sulfur, or in which at least one hydrogen may be substitued by fluorine or chlorine,

A^1, A^2, A^3, and A^4 each independently represents a group selected from the group consisting of

(a) a trans-1,4-cyclohexylene group (in which one CH_2 group or two CH_2 groups that are not adjacent to each other may be substituted by oxygen or sulfur),

(b) a 1,4-phenylene group (in which at least one CH group may be substituted by nitrogen), and

(c) a 1,4-cyclohexenylene group, a 1,4-bicyclo[2.2.2]octylene group, a piperidine-1,4-diyl group, a naphthalene-2,6-diyl group, a decahydronaphthalene-2,6-diyl group or a 1,2,3,4-tetrahydronaphthalene-2,6-diyl group,

the above-mentioned group (a), group (b), and group (c) may be substituted by -CN or a

halogen,

Z^1, Z^2, Z^3, and Z^4 each independently represents $-CH_2CH_2-$, $-CH=CH-$, $-CH(CH_3)CH_2-$, $-CH_2CH(CH_3)-$, $-CH(CH_3)CH(CH_3)-$, $-CF_2CF_2-$, $-CF=CF-$, $-CH_2O-$, $-OCH_2-$, $-OCH(CH_3)-$, $-CH(CH_3)O-$, $-(CH_2)_4-$, $-(CH_2)_3O-$, $-O(CH_2)_3$, $-C\equiv C-$, $-CF_2O-$, $-OCF_2-$, -COO-, -OCO, -COS, -SCO-, or a single bond,

when A^1, A^2, A^3, A^4, Z^1, Z^2, Z^3, and Z^4 exist in plural, they may be identical to each other or different from each other,

a, b, c, and d each independently represents 0, 1 or 2, and

W^1 and W^2 each independently represents fluorine, chlorine, $-CF_3$, $-CF_2H$, $-OCF_3$, or $-OCF_2H$).

[Claim 2]

A compound according to claim 1, wherein R^1 and R^2 each independently represents an alkyl group having 1 to 7 carbon atoms or an alkenyl group having 2 to 7 carbon atoms (in which one CH_2 group may be substituted by an oxygen atom), and both W^1 and W^2 represent a fluorine atom in the general formula (1).

[Claim 3]

A compound according to claim 1, wherein A^1, A^2, A^3 and A^4 each independently represents a trans1,4-cyclohexylene group, a 1,4-phenylene group which may be substituted by at least one fluorine atom, or a 1,4-bicyclo[2.2.2]octylene group in the general formula (1).

[Claim 4]

A compound according to claim 1, wherein Z^1, Z^2, Z^3, and Z^4 each independently represents $-CH_2CH_2-$, $-CH=CH-$, $-CF_2CF_2-$, $-CF=CF-$, $-CH_2O-$, $-OCH_2-$, $-C\equiv C-$, $-CF_2O-$, $-OCF_2-$ or a single bond in the general formula (1).

[Claim 5]

A compound according to claim 1, wherein the sum of a, b, c, and d is 1, 2 or 3 in the general formula (1).

[Claim 6]

A compound according to claim 1, wherein R^1 and R^2 each independently represents an alkyl group having 1 to 7 carbon atoms or an alkenyl group having 2 to 7 carbon atoms (in which a CH_2 group may be substituted by oxygen), both W^1 and W^2 represent fluorine atoms, A^1, A^2, A^3, and A^4 each independently represents a trans-1,4-cyclohexylene group, a 1,4-phenylene group which may be substituted by at least one fluorine atom, or a 1,4-bicyclo[2.2.2]octylene group, Z^1, Z^2, Z^3 and Z^4 each independently represents $-CH_2CH_2-$, $-CH=CH-$, $-CF_2CF_2-$, $-CF=CF-$, $-CH_2O-$, $-OCH_2-$, $-C\equiv C-$, $-CF_2O-$, $-OCF_2-$, or a single bond, and the sum of a, b, c, and d is 1, 2 or 3 in the general formula (1).

[Claim 7]

A liquid crystal composition comprising at least one compound of any one of claims 1 to 6.

[Claim 8]

A liquid crystal composition according to claim 7, comprising at least one compound represent by general formula (2):

[Chemical Formula 2]

$$R^3-B^1-Y^1-(B^2-Y^2)_p-R^4 \qquad (2)$$

(wherein,

R^3 and R^4 each independently represents the same meaning as that of R^1 in the general formula (1) of claim 1,

B^1 and B^2 each independently represents the same meaning as that of A^1 in the general formula (1) of claim 1,

Y^1 and Y^2 each independently represents the same meaning as that of Z^1 in the general formula (1) of claim 1,

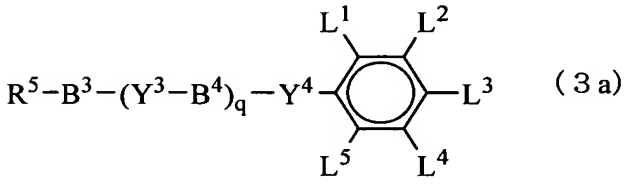
when Y^2 and B^2 exist in plural, they may be identical to each other or different from each other, and

p represents 0, 1 or 2).

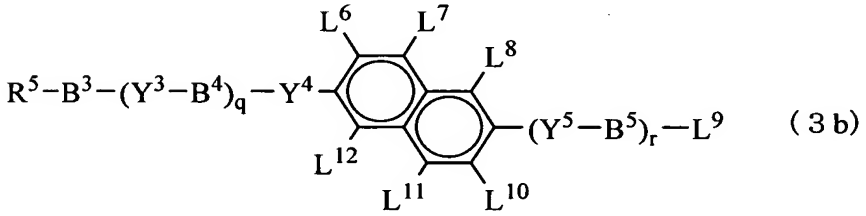
[Claim 9]

A liquid crystal composition according to claim 7, comprising at least one compound selected from the group consisting of compounds represented by general formula (3a), general formula (3b), and general formula (3c):

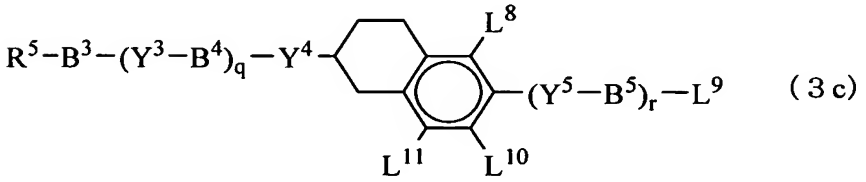
[Chemical Formula 3]



(3a)



(3b)



(3c)

(wherein

R^5 represents the same meaning as in R^1 in the general formula (1) of claim 1,

B^3, B^4, and B^5 each independently represents the same meaning as that of A^1 in the

general formula (1) of claim 1,

Y^3, Y^4, and Y^5 each independently represents the same meaning as in Z^1 in the general formula (1) of claim 1,

L^1, L^2, L^4, L^5, L^6, L^7, L^8, L^{10}, L^{11}, and L^{12} each independently represents hydrogen or fluorine,

q and r each independently represents 0, 1, or 2, provided that the sum of q and r is no more than 2, and

L^3 and L^9 each independently represents hydrogen, fluorine, chlorine, -CN, $-CF_3$, $-OCH_2F$, $-OCHF_2$, $-OCF_3$, $-CH_2CF_3$, or the same meaning as R^1 of claim 1).

[Claim 10]

A liquid crystal composition according to claim 7, comprising at least one compound selected from the group consisting of compounds represented by the general formula (2) of claim 8 and at least one compound selected from the group consisting of compounds represented by the general formula (3a), general formula (3b) and general formula (3c) of claim 9.

[Claim 11]

A liquid crystal composition according to any one of claims 7 to 10, wherein a content ratio of the compound represented by the general formula (1) is within a range from 2 to 30% by mass.

[Claim 12]

A liquid crystal composition according to any one of claims 7 to 10, wherein the liquid crystal composition has a negative dielectric anisotropy value.

[Claim 13]

A liquid crystal display element using the liquid crystal composition of any one

of claims 7 to 12.

[Claim 14]

A liquid crystal display element according to claim 13, wherein the liquid crystal display element has an active matrix drive system.

[Claim 15]

A liquid crystal display element according to claim 14, displayed in vertical alignment mode.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a chroman derivative, a liquid crystal composition using this, and a liquid crystal display element using this.

[0002]

[Prior Art]

At present, liquid crystal display elements are now widely used due to their excellent characteristics such as low voltage actuation, thin model display, or the like. Examples of the display systems of conventional liquid crystal display elements, particularly small-to-medium-sized elements, include TN (twisted nematic), STN (super twisted nematic), active matrix based on TN (TFT : thin film transistor), and the like, and they utilize liquid crystal compositions having positive dielectric anisotropy values.

[0003]

However, these display systems have a narrow viewing angle as one of their defects, and an improvement thereof has become a major issue in accordance with the currently increasing demand for larger liquid crystal panels. As a solution to this, display systems such as vertical alignment mode, IPS (In Plane Switching), and the like have recently been newly put to practical use. The vertical alignment mode is a system to improve the viewing angle by utilizing vertical alignment of liquid crystal molecules, in which a liquid crystal composition having a negative dielectric anisotropy value is used. IPS is a system to improve the viewing angle by switching liquid crystal molecules using a horizontal electric field in parallel with glass substrates, in which a liquid crystal composition having a positive or negative dielectric anisotropy value is

used. Thus, the vertical alignment mode and IPS, which are display systems effective for improving the viewing angle, require liquid crystal compounds and liquid crystal compositions having negative dielectric anisotropy values, which have become strongly demanded. However, liquid crystal compounds or liquid crystal compositions having negative dielectric anisotropy values have not been sufficiently developed, because conventional display systems mainly use liquid crystal compositions having positive dielectric anisotropy values as described above.

[0004]

As a liquid crystal compound having a negative dielectric anisotropy value, a liquid crystal compound having a 2,3-difluorophenylene skeleton (see Patent Document 1) and a liquid crystal compound having a 3,4-difluoro-5,6,7,8-tetrahydronaphthalene skeleton (see Patent Document 2) are disclosed. However, the absolute values of the dielectric anisotropy values of these compounds are not necessarily sufficiently large, which prevents the progress of the development of liquid crystal display elements, so a compound having a large absolute value of negative dielectric anisotropy value is required to be developed.

[0005]

[Patent Document 1] German Laid-Open Patent Application No. 19522145

[Patent Document 2] German Laid-Open Patent Application No. 3906058

[0006]

[Problems to be Solved by the Invention]

The object of the present invention is to provide a liquid crystal compound having a large absolute value of negative dielectric anisotropy and to provide a liquid crystal element composition and a liquid crystal display element using the same.

[0007]

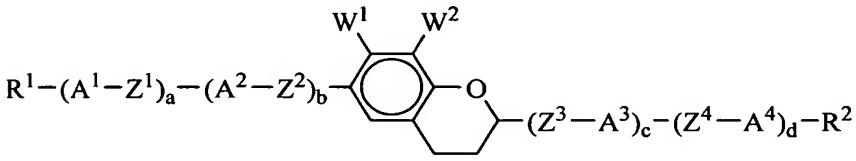
[Means for Solving the Problem]

As a result of examination with respect to chroman derivatives and nematic liquid crystal compositions using the same, the inventors of the present invention have completed the following invention.

[0008]

The present invention provides a chroman derivative, represented by general formula (1):

[Chemical Formula 4]



(1)

(wherein R^1 and R^2 each independently represents hydrogen, an alkyl group having 1 to 12 carbon atoms or an alkenyl group having 2 to 12 carbon atoms, in which one CH_2 group or at least two CH_2 groups that are not adjacent to each other may be substituted by oxygen or sulfur, or in which at least one hydrogen may be substitued by fluorine or chlorine,

[0009]

A^1, A^2, A^3, and A^4 each independently represents a group selected from the group consisting of

(a) a trans-1,4-cyclohexylene group (in which one CH_2 group or two CH_2 groups that are not adjacent to each other may be substituted by oxygen or sulfur),

(b) 1,4-phenylene group (in which at least one CH group may be substituted by nitrogen),

(c) 1,4-cyclohexenylene group, 1,4-bicyclo[2.2.2]octylene group, piperidine-1,4-diyl

group, naphthalene-2,6-diyl group, decahydronaphthalene-2,6-diyl group or 1,2,3,4-tetrahydronaphthalene-2,6-diyl group,

the above-mentioned group (a), group (b), and group (c) may be substituted by -CN or a halogen,

Z^1, Z^2, Z^3, and Z^4 each independently represents $-CH_2CH_2-$, $-CH=CH-$, $-CH(CH_3)CH_2-$, $-CH_2CH(CH_3)-$, $-CH(CH_3)CH(CH_3)-$, $-CF_2CF_2-$, $-CF=CF-$, $-CH_2O-$, $-OCH_2-$, $-OCH(CH_3)-$, $-CH(CH_3)O-$, $-(CH_2)_4-$, $-(CH_2)_3O-$, $-O(CH_2)_3$, $-C\equiv C-$, $-CF_2O-$, $-OCF_2-$, -COO-, -OCO, -COS, -SCO-, or a single bond, when A^1, A^2, A^3, A^4, Z^1, Z^2, Z^3, and Z^4 exist in plural, they may be identical to each other or different from each other,

a, b, c, and d each independently represents 0, 1, or 2, and

W^1 and W^2 each independently represents fluorine, chlorine, $-CF_3$, $-CF_2H$, $-OCF_3$, or $-OCF_2H$), and

a liquid composition using the same and a liquid crystal display element using the same.

[0010]

[Preferred Example of the Invention]

Although the compound represented by general formula (1) covers many compounds, the following compounds are preferable.

[0011]

It is preferable that in general formula (1) R^1 and R^2 each independently represents an alkyl group having 1 to 12 carbon atoms, an alkenyl group having 2 to 12 carbon atoms, an alkoxyl group having 1 to 12 carbon atoms, an alkyl group having 1 to 7 carbon atoms which is substituted by an alkoxyl group having 1 to 5 carbon atoms, or an alkenyl group having 2 to 7 carbon atoms which is substituted by an alkoxyl group having 1 to 5 carbon atoms, and more preferably represents an alkyl group having 1 to 12

carbon atoms, or an alkenyl group having 2 to 12 carbon atoms, and specifically represents $-CH_3$, $-CH_2CH_3$, $-(CH_2)_2CH_3$, $-(CH_2)_3CH_3$, $-(CH_2)_4CH_3$, $-(CH_2)_5CH_3$, $-(CH_2)_6CH_3$, $-(CH_2)_7CH_3$, $-CH=CH_2$, $-CH=CHCH_3$ (E form), $-(CH_2)_2CH=CH_2$, $-(CH_2)_2CH=CHCH_3$ (E form), $-(CH_2)_4CH=CH_2$, $-(CH_2)_4CH=CHCH_3$ (E form), or $-(CH_2)_6CH=CH_2$.

[0012]

It is preferable that A^1, A^2, A^3 and A^4 each independently represents a trans-1,4-cyclohexylene group (including one in which one CH_2 group or two CH_2 groups that are not adjacent to each other are substituted by oxygen), 1,4-phenylene group (including one in which at least one CH group is substituted by nitrogen), 1,4-cyclohexenylene group,1,4-bicyclo[2.2.2]octylene group, piperidine-1,4-diyl group, naphthalene-2,6-diyl group, decahydronaphthalene-2,6-diyl group, 1,2,3,4-tetrahydronaphthalene-2,6-diyl group, or a substituent in which a hydrogen atom of the above-mentioned group is substituted by fluorine, and more preferably represents a trans-1,4-cyclohexylene group, 1,4-phenylene group, 1,4-phenylene group substituted by fluorine or 1,4-bicyclo[2.2.2]octylene group.

[0013]

It is preferable that Z^1 ,Z^2 ,Z^3 and Z^4 each independently represents $-CH_2CH_2-$, $-CH=CH-$ (E form), $-CH(CH_3)CH_2-$, $-CH_2CH(CH_3)-$, $-CH(CH_3)CH(CH_3)-$,$-CF_2CF_2-$, $-CF=CF-$ (E form), $-CH_2O-$, $-OCH_2-$, $-OCH(CH_3)-$, $-CH(CH_3)O-$, $-(CH_2)_4-$, $-(CH_2)_3O-$, $-O(CH_2)_3-$, $-C\equiv C-$, $-CF_2O-$, $-OCF_2-$, $-COO-$, $-OCO-$, $-COS-$, $-SCO-$or a single bond, and more preferably represents $-CH_2CH_2-$, $-CH=CH-$ (E form), $-CH(CH_3)CH_2-$, $-CH_2CH(CH_3)-$, $-CF_2CF_2-$, $-CF=CF-$ (E form), $-CH_2O-$, $-OCH_2-$, $-OCH(CH_3)-$, $-CH(CH_3)O-$, $-C\equiv C-$, $-CF_2O-$, $-OCF_2-$ or a single bond, and even more preferably

represents $-CH_2CH_2-$, -CH=CH- (E form) or a single bond.

[0014]

It is preferable that W^1 and W^2 each independently represents fluorine, chlorine, $-CF_3$, $-CF_2H$, $-OCF_3$ or $-OCF_2H$, and more preferably represents fluorine or chlorine, and particularly preferably represents fluorine.

[0015]

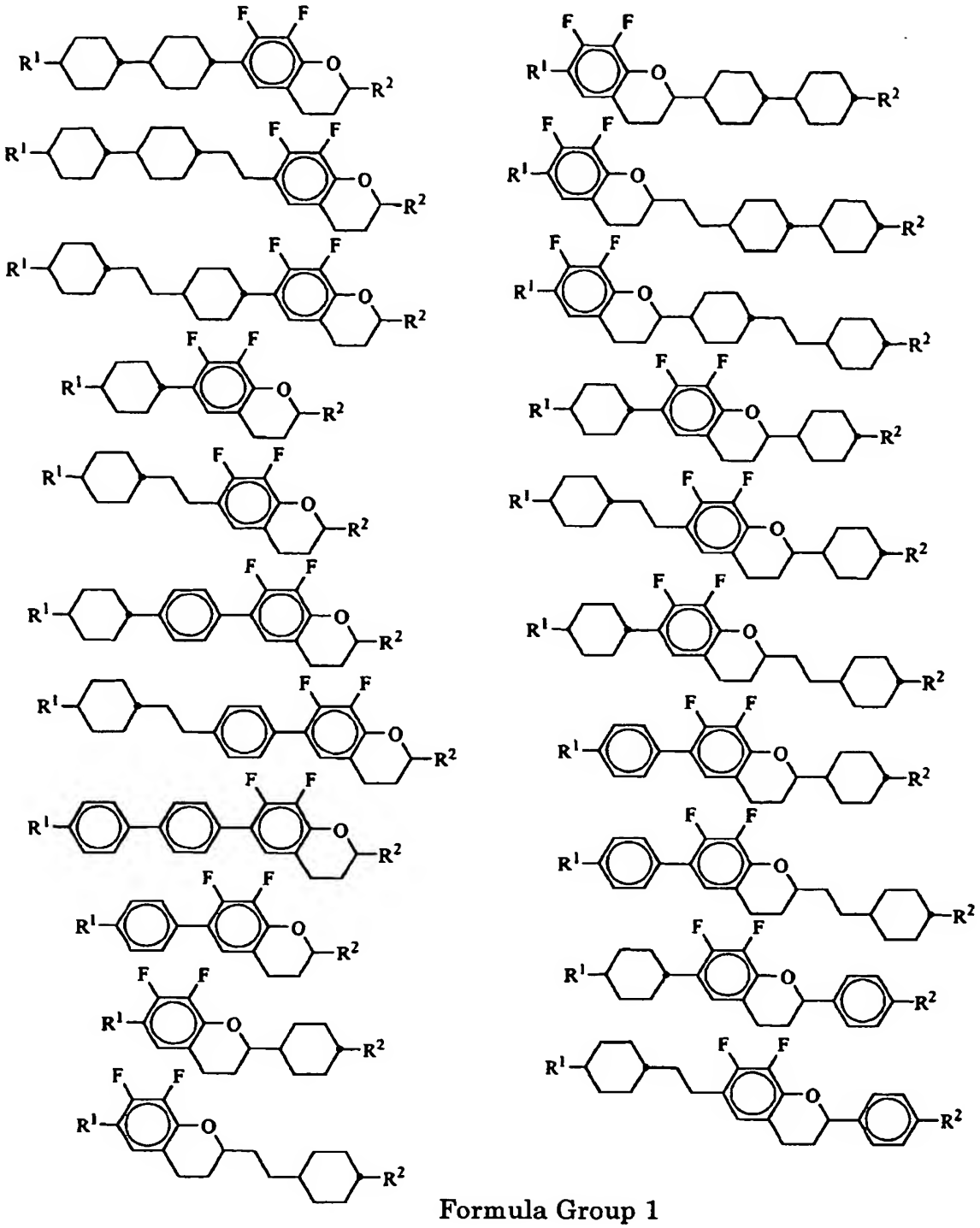
Although a, b, c, and d each independently represents 0, 1 or 2, it is preferable that the sum of a, b, c, and d is no less than 1 and no more than 3, and more preferably no less than 1 and no more than 2.

[0016]

In more detail, among the compounds represented by general formula (1), as particularly preferable compounds, compounds shown in formula group (1) can be mentioned.

[0017]

[Chemical Formula 5]



Formula Group 1

[0018]

(In the formulae, R^1 and R^2 each independently represents $-CH_3$, $-CH_2CH_3$,

$-(CH_2)_2CH_3$, $-(CH_2)_3CH_3$, $-(CH_2)_4CH_3$, $-(CH_2)_5CH_3$, $-(CH_2)_6CH_3$, $-(CH_2)_7CH_3$, $-CH=CH_2$, $-CH=CHCH_3$ (E form), $-(CH_2)_2CH=CH_2$, $-(CH_2)_2CH=CHCH_3$ (E form), $-(CH_2)_4CH=CH_2$, $-(CH_2)_4CH=CHCH_3$ (E form), or $-(CH_2)_6CH=CH_2$).

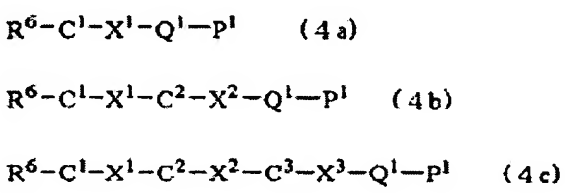
[0019]

It is preferable that the composition according to the present invention contains at least one compound represented by the general formula (1) as the first component and at least one of the following second and third components in particular as additional components of nematic liquid crystal compounds preferably mixed with the compound represented by the general formula (1).

[0020]

That is, the second component is a so-called fluorinated (halogenated) liquid crystal compound, and contains compounds represented by the following general formulae (4a) to (4c).

[Chemical Formula 6]



$$R^6-C^1-X^1-Q^1-P^1 \quad (4a)$$

$$R^6-C^1-X^1-C^2-X^2-Q^1-P^1 \quad (4b)$$

$$R^6-C^1-X^1-C^2-X^2-C^3-X^3-Q^1-P^1 \quad (4c)$$

[0021]

In the above formulae, R^6 represents an alkyl group of 1 to 12 carbon atoms, which may be a straight chain, or contain methyl or ethyl branches, a 3 to 6 membered ring structure, an optional $-CH_2-$ replaced by a -O-, -CH=CH-, -CH=CF-, -CF=CH-, -CF=CF- or -C≡C-, or an optional hydrogen atom substituted with a fluorine atom or a trifluoromethoxy group, and preferably represents a straight chain alkyl group of 2 to 7

carbon atoms, straight chain 1-alkenyl group of 2 to 7 carbon atoms, straight chain 3-alkenyl group of 4 to 7 carbon atoms, or alkyl group of 1 to 5 carbon atoms having a terminal substituted with an alkoxyl group of 1 to 3 carbon atoms. Furthermore, when branching leads to an asymmetric carbon atom, the compound may be an optically active form or a racemic form.

[0022]

C^1, C^2 and C^3 each independently represent a trans-1,4-cyclohexylene group, a transdecahydronaphthalene-trans-2,6-diyl group, a 1,4-phenylene group which may be substituted with one or more fluorine atoms, a naphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms, a tetrahydronaphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms, a 1,4-cylohexenylene group which may be substituted with a fluorine atom, a 1,3-dioxane-trans-2,5-diyl group, a pyrimidine-2,5-diyl group or a pyridine-2,5-diyl group, and preferably represents a trans-1,4-cyclohexylene group, a transdecahydronaphthalene-trans-2,6-diyl group, a naphthalene-2,6-diyl group which may be substituted with a fluorine atom or a 1,4-phenylene group which may be substituted with one or two fluorine atoms. Particularly, when C^2 is a trans-1,4-cyclohexylene group or a transdecahydronaphthalene-trans-2,6-diyl group, it is preferable that C^1 is a trans-1,4-cyclohexylene group. When C^3 is a trans-1,4-cyclohexylene group or a transdecahydronaphthalene-trans-2,6-diyl group, it is preferable that C^2 and C^1 are trans-1,4-cyclohexylene groups. Furthermore in (4C), it is preferable that C^1 is a trans-1,4-cyclohexylene group.

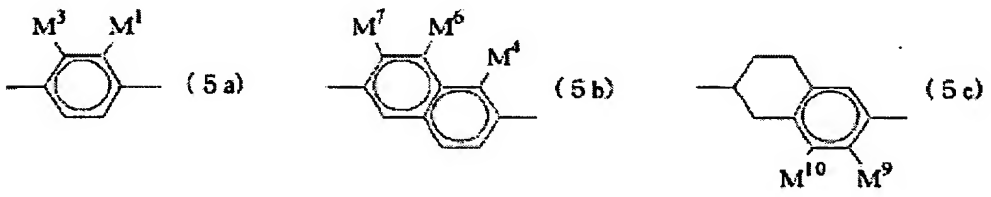
X^1, X^2 and X^3 are linkage groups, and each independently represents a single bond, an ethylene group ($-CH_2CH_2-$), a 1,2-propylene group ($-CH(CH_3)CH_2-$ and

$-CH_2CH(CH_3)-$), a 1,4-butylene group, -COO-, -OCO-, $--OCF_2-$, $-CF_2O-$, -CH=CH-, -CH=CF-, -CF=CH-, -CF=CF-, -C≡C- or –CH=NN=CH-, preferably represents a single bond, an ethylene group, a 1,4-butylene group, -COO-, $-OCF_2-$, $-CF_2O-$, -CF=CF- or--C≡C-, and more preferably represents a single bond or an ethylene group. Furthermore, it is preferable that at least one of these linkage groups in (4b), and at least two of the linkage groups in (4c) be single bonds.

[0023]

Q^1 is an aromatic ring, and can be represented by the general formulae (5a) to (5c) shown below.

[Chemical Formula 7]



[0024]

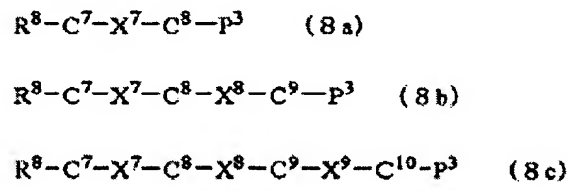
In the formulae, M^1 to M^{10} each independently represent a hydrogen atom or a fluorine atom, although in (5a) it is preferable that at least one of M^1 and M^3 be a fluorine atom, and more preferably both M^1 and M^3 be fluorine atoms. In (5b), it is preferable that at least one of M^4, M^6 and M^7 be a fluorine atom, more preferably at least two of M^4, M^6 and M^7 be fluorine atoms, even more preferably all of M^4, M^6 and M^7 be fluorine atoms.

The terminal group P^1 represents an alkoxyl group, alkyl group, alkenyl group or alkenyloxy group.

[0025]

The third component is a non-polar liquid crystal having an approximately 0 dielectric anisotropy value, and contains compounds represented by the general formulae (8a) to (8c) shown below.

[Chemical Formula 8]



$$R^8-C^7-X^7-C^8-P^3 \quad (8a)$$

$$R^8-C^7-X^7-C^8-X^8-C^9-P^3 \quad (8b)$$

$$R^8-C^7-X^7-C^8-X^8-C^9-X^9-C^{10}-P^3 \quad (8c)$$

[0026]

In the above formulae, R^8 and P^3 each independently represents an alkyl group of 1 to 12 carbon atoms, which may be a straight chain, or contain methyl or ethyl branches, a 3 to 6 membered ring structure, an optional $-CH_2-$ replaced by -O-, -CH=CH-, -CH=CF-, -CF=CH-, -CF=CF- or -C≡C-, or an optional hydrogen atom substituted with a fluorine atom or a trifluoromethoxy group, and preferably represents a straight chain alkyl groups of 1 to 7 carbon atoms, straight chain 1-alkenyl group of 2 to 7 carbon atoms, straight chain 3-alkenyl group of 4 to 7 carbon atoms, straight chain alkoxyl group of 1 to 3 carbon atoms, or straight chain alkyl groups of 1 to 5 carbon atoms having a terminal substituted with an alkoxyl group of 1 to 3 carbon atoms. Furthermore, it is particularly preferable that at least one of them be a straight chain alkyl group of 1to 7 carbon atoms, straight chain 1-alkenyl groups of 2 to 7 carbon atoms or straight chain 3-alkenyl groups of 4 to 7 carbon atoms.

[0027]

C^7, C^8 and C^9 each independently represents a trans-1,4-cyclohexylene group, a

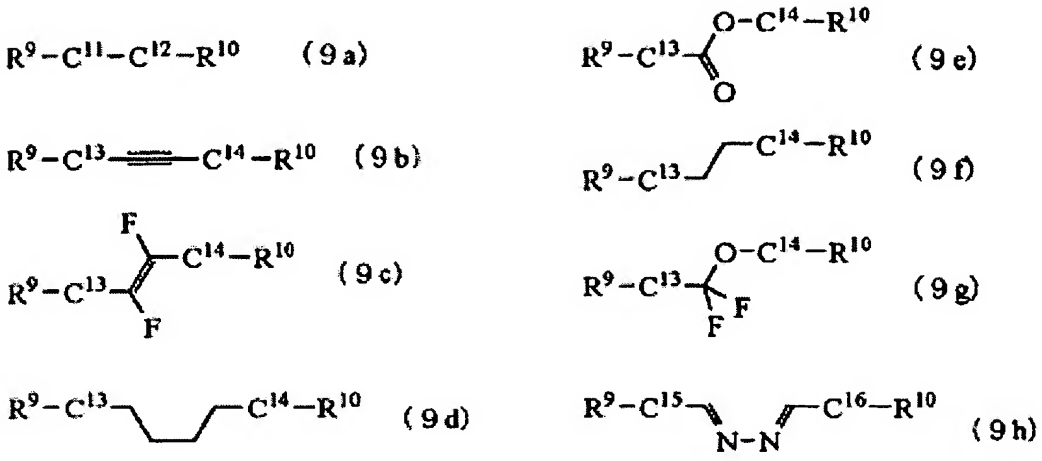
transdecahydronaphthalene-trans-2,6-diyl group, a 1,4-phenylene group which may be substituted with one or two fluorine atoms or methyl groups, a naphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms, a tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms, a 1,4-cylohexenylene group which may be substituted with one or two fluorine atoms, a 1,3-dioxane-trans-2,5-diyl group, a pyrimidine-2,5-diyl group or a pyridine-2,5-diyl group. It is preferable that each compound has one or less of a transdecahydronaphthalene-trans-2,6-diyl group, naphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms, tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms, 1,4-cylohexenylene group which may be substituted with fluorine atoms, 1,3-dioxane-trans-2,5-diyl group, pyrimidine-2,5-diyl group and pyridine-2,5-diyl group, and another ring selected from a trans-1,4-cyclohexylene group and a 1,4-phenylene group which may be substituted with one or two fluorine atoms or methyl groups.

X^7, X^8 and X^9 are linkage groups, and each independently represents a single bond, an ethylene group ($-CH_2CH_2-$), a 1,2-propylene group ($-CH(CH_3)CH_2-$ and $-CH_2CH(CH_3)-$), a 1,4-butylene group, -COO-, -OCO-, $-OCF_2-$, $-CF_2O-$, -CH=CH-, -CH=CF-, -CF=CH-, -CF=CF-, -C≡C- or –CH=NN=CH-, preferably represents a single bond, an ethylene group, a 1,4-butylene group, -COO-, -OCO-, $-OCF_2-$, $-CF_2O-$, --CF=CF-, -C≡C-, or –CH=NN=CH-. It is preferable that at least one of the linkage groups in (8b) and at least two of the linkage groups in (8c) be single bonds.

[0028]

Preferred aspects of (8a) are represented by the following general formulae (9a) to (9h).

[Chemical Formula 9]



[0029]

In the above formulae, R^9 and R^{10} each independently represents a straight chain alkyl group of 1 to 7 carbon atoms, a straight chain 1-alkenyl groups of 2 to 7 carbon atoms, a straight chain 3-alkenyl groups of 4 to 7 carbon atoms, a straight chain alkoxyl group of 1 to 3 carbon atoms, or alkyl group of 1 to 5 carbon atoms in which the terminal is substituted with an alkoxyl group of 1 to 3 carbon atoms, provided that at least one of them represents a straight chain alxyl group of 1 to 7 carbon atoms, a straight chain 1-alkenyl groups of 2 to 7 carbon atoms, or a straight chain 3-alkenyl groups of 4 to 7 carbon atoms. However, when C^{11}, C^{13} and C^{15} are aromatic rings, the corresponding R^9 is not a 1-alkenyl group nor alkoxyl group, and when C^{12}, C^{14} and C^{16} are aromatic rings, the corresponding R^{10} is not a 1-alkenyl group nor alkoxyl group.

[0030]

$C^{11}$and C^{12} each independently represents a trans-1,4-cyclohexylene group, a transdecahydronaphthalene-trans-2,6-diyl group, a 1,4-phenylene group which may be substituted with one or two fluorine atoms or methyl groups, a naphthalene-2,6-diyl

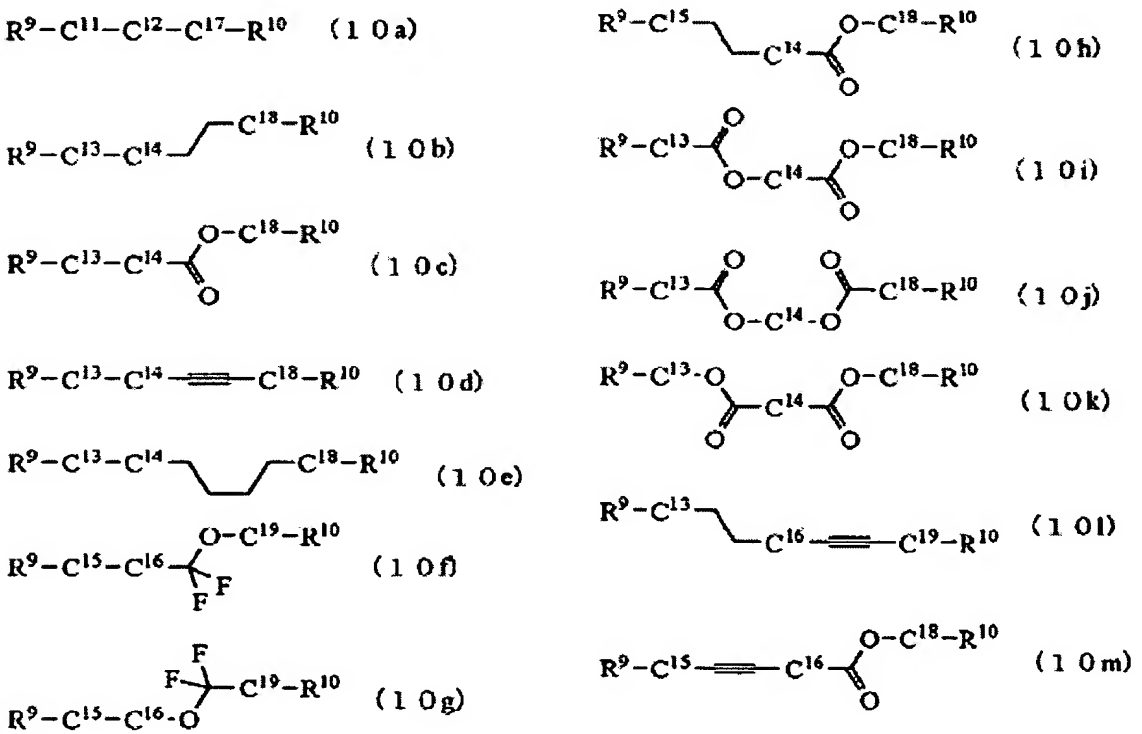
group which may be substituted with one or more fluorine atoms, a tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms, a 1,4-cylohexenylene group which may be substituted with one or two fluorine atoms, a 1,3-dioxane-trans-2,5-diyl group, a pyrimidine-2,5-diyl group or a pyridine-2,5-diyl group. It is preferable that each compound has one or less of a transdecahydronaphthalene-trans-2,6-diyl group, naphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms, tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms, 1,4-cylohexenylene group which may be substituted with fluorine atoms, 1,3-dioxane-trans-2,5-diyl group, and pyrimidine-2,5-diyl group or pyridine-2,5-diyl group, and another ring selected from a trans-1,4-cyclohexylene group and a 1,4-phenylene group which may be substituted with one or two fluorine atoms or methyl groups. $C^{13}$and C^{14} each independently represents a trans-1,4-cyclohexylene group, a transdecahydronaphthalene-trans-2,6-diyl group, a 1,4-phenylene group which may be substituted with one or two fluorine atoms or methyl groups, a naphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms, or a tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms, although it is preferable that each compound has one or less of a transdecahydronaphthalene-trans-2,6-diyl group, naphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms, and tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms, and another ring selected from a trans-1,4-cyclohexylene group and a 1,4-phenylene group which may be substituted with one or two fluorine atoms or methyl groups. C^{15} and C^{16} each independently represents a 1,4-phenylene group which may be substituted with one or two fluorine atoms or methyl groups, a naphthalene-2,6-diyl group which may be substituted with one

or more fluorine atoms or a tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms, although it is preferable that each compound has one or less of a naphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms and a tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms.

[0031]

Preferred aspects of (8b) are represented by the following general formulae (10a) to (10m).

[Chemical Formula 10]



[0032]

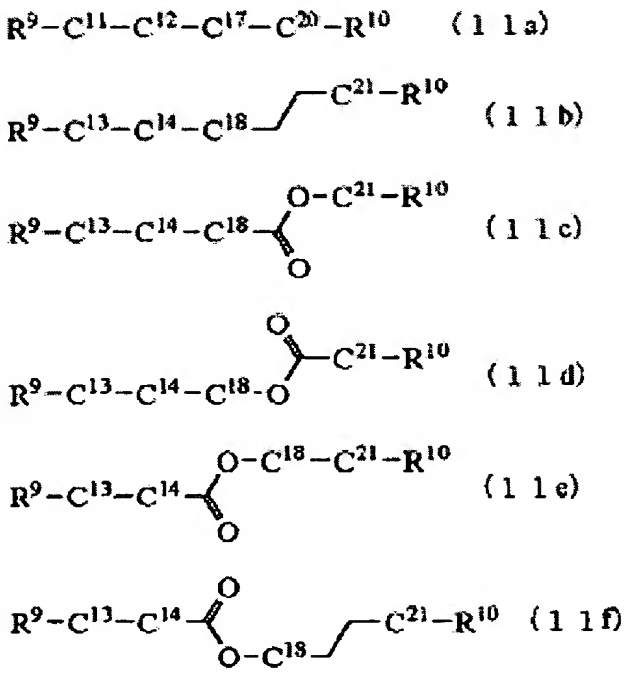
In the above formulae, C^{11}, C^{12}, C^{13}, C^{14}, C^{15} and C^{16} represent the same meaning as the above, and pairs of C^{17} and C^{11}, C^{18} and C^{13}, and C^{19} and C^{15} each

represent the same meaning. In addition, in each above compound, it is preferable that one or less of a transdecahydronaphthalene-trans-2,6-diyl group, a naphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms, a tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms, a 1,4-cylohexenylene group which may be substituted with fluorine atoms, a 1,3-dioxane-trans-2,5-diyl group, a pyrimidine-2,5-diyl group and a pyridine-2,5-diyl group be contained, and the other ring in such a case be a trans-1,4-cyclohexylene group or a 1,4-phenylene group which may be substituted with one or two fluorine atoms or methyl groups.

[0033]

Next, preferred aspects of (8c) are represented by the following general formulae (11a) to (11f).

[Chemical Formula 11]



[0034]

In the above formulae, C^{11}, C^{12}, C^{13}, C^{14}, C^{17} and C^{18} represent the same meaning as the above, and pairs of C^{20} and C^{11}, and C^{21} and C^{13} each represents the same meaning. In addition, in each above compound, it is preferable that one or less of a transdecahydronaphthalene-trans-2,6-diyl group, a naphthalene-2,6-diyl group which may be substituted with one or more fluorine atoms, a tetrahydronaphthalene-2,6-diyl group which may be substituted with one or two fluorine atoms, a 1,4-cylohexenylene group which may be substituted with fluorine atoms, a 1,3-dioxane-trans-2,5-diyl group, a pyrimidine-2,5-diyl group and a pyridine-2,5-diyl group be contained, and the other ring be a trans-1,4-cyclohexylene group or a 1,4-phenylene group which may be substituted with one or two fluorine atoms or methyl groups.

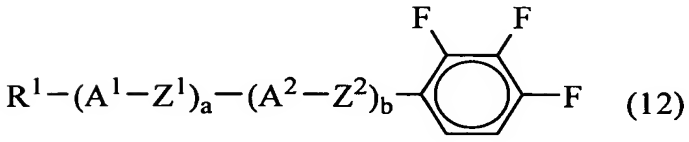
In the present invention, examples of preparation methods of the compounds represented by the general formula (1) are shown in the following. However, the purport and range of application of the present invention is of course not limited to these preparation method examples.

[0035]

(Preparation Method 1)

Into a benzene derivative represented by general formula (12)

[Chemical Formula 12]



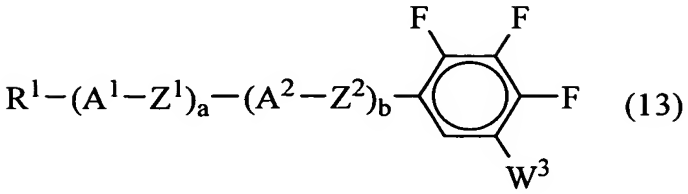
(12)

(wherein R^1, A^1, A^2, Z^1, Z^2, a, and b each independently represents the same meaning as that of general formula (1)), a halogen group is introduced to produce a benzene

derivative represented by general formula (13)

[0036]

[Chemical Formula 13]



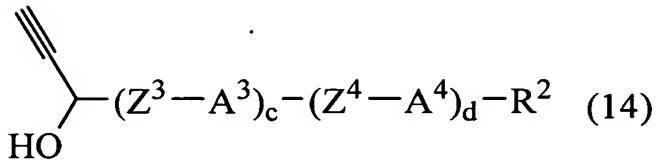
(13)

(wherein R^1, A^1, A^2, Z^1, Z^2, a, and b each independently represents the same meaning as that of general formula (1), and W3 represents halogen). In such a case, W3 preferably is chlorine, bromine, or iodine, and more preferably iodine.

[0037]

With the produced compound represented by general formula (13), an acetylene derivative represented by general formula (14)

[Chemical Formula 14]

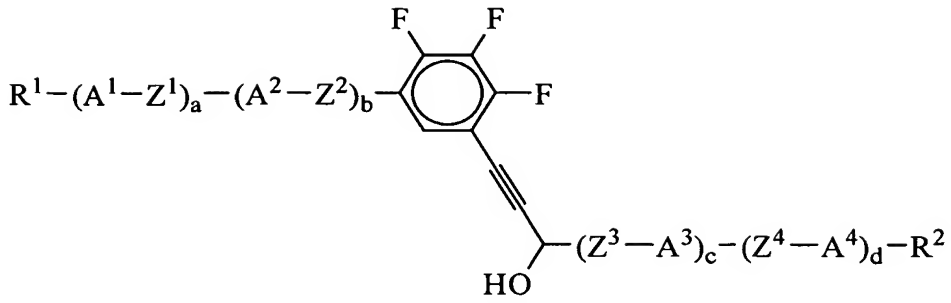


(14)

(wherein R^2, A^3, A^4, Z^3, Z^4, c, and d each independently represents the same meaning as that of general formula (1)) is coupling-reacted to produce an acetylene derivative represented by general formula (15)

[0038]

[Chemical Formula 15]



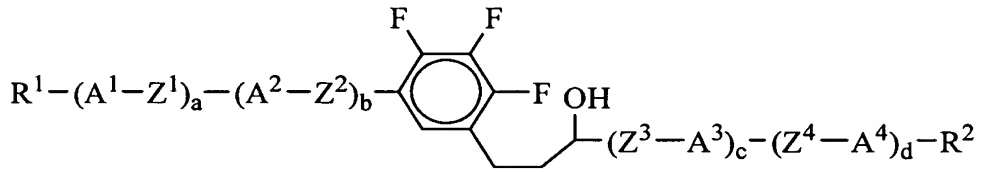
(15)

(wherein R^1, R^2, A^1, A^2, A^3, A^4, Z^1, Z^2, Z^3, Z^4, a, b, c, and d each independently represents the same meaning as that of general formula (1)).

[0039]

The produced compound represented by general formula (15) is hydrogenated to produce an alcohol derivative represented by general formula (16)

[Chemical Formula 16]



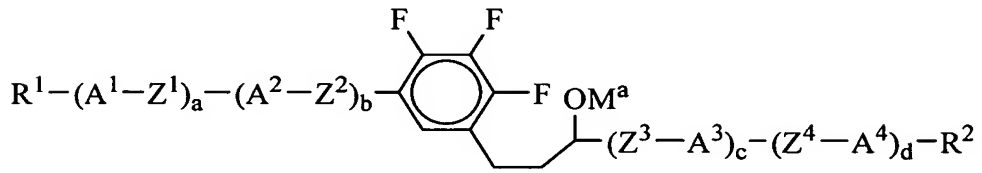
(16)

(wherein R^1, R^2, A^1, A^2, A^3, A^4, Z^1, Z^2, Z^3, Z^4, a, b, c, and d each independently represents the same meaning as that of general formula (1)).

[0040]

The produced compound represented by general formula (16) is reacted with a base to produce an alcoholate represented by general formula (17)

[Chemical Formula 17]



(17)

[0041]

(wherein R^1, R^2, A^1, A^2, A^3, A^4, Z^1, Z^2, Z^3, Z^4, a, b, c, and d each independently represents the same meaning as that of general formula (1), and M^a

represents an alkali metal such as lithium, sodium, potassium or the like, an alkaline earth metal such as magnesium, calcium, or the like). Preferable examples of the base include metal hydrides, metal carbonates, metal hydroxides, metal carboxylates, metal amides, metals, and the like. Among them, alkali metal hydrides, alkali metal carbonates, alkali metal hydroxides, alkali metal amides, and alkali metals are preferable, and alkali metal hydrides and alkali metal carbonates are more preferable. Preferable examples of alkali metal hydrides include lithium hydride, sodium hydride, and potassium hydride, and preferable examples of alkali metal carbonates include sodium carbonate, sodium hydrogencarbonate, potassium carbonate, and potassium hydrogencarbonate.

[0042]

In such a case, although any solvents can be used provided that they enable the reaction to proceed preferably, ether solvents, hydrocarbon solvents, aromatic solvents, polar solvents, or the like can be preferably used. Preferable examples of the ether solvents include 1,4-dioxane, 1,3-dioxane, tetrahydrofuran, diethylether, t-butylmethylether, and the like. Preferable examples of chlorine solvents include dichloromethane, 1,2- dichloroethane, carbon tetrachloride, and the like. Preferable examples of the hydrocarbon solvents include pentane, hexane, cyclohexane, heptane, octane, and the like. Preferable examples of the aromatic solvents include benzene, toluene, xylene, mesitylene, chlorobenzene, dichlorobenzene, and the like. Preferable examples of the polar solvents include N,N-dimethylformamide, N-methylpyrrolidone, dimethylsulfoxide, sulfolane, and the like. Among them, the ether solvents such as tetrahydrofuran, dimethylether, and the like, and the polar solvents such as N,N-dimethylformamide and the like are more preferable. The above-mentioned

solvents may be used singularly or in combination of two or more.

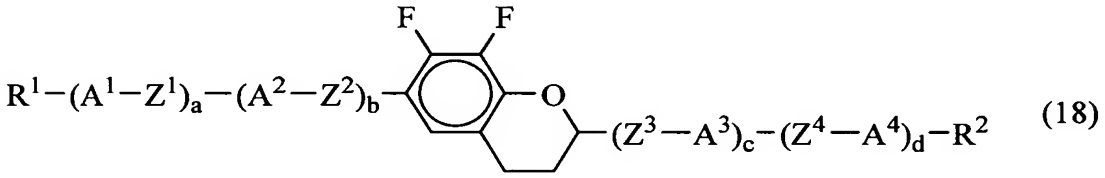
[0043]

The reaction temperature may be set within a range from a melting point to a reflux temperature of the solvent, and is preferably -20°C to 60°C.

[0044]

The produced compound represented by general formula (17) is intramolecular-substituted to produce a chroman derivative represented by general formula (18)

[Chemical Formula 18]



(18)

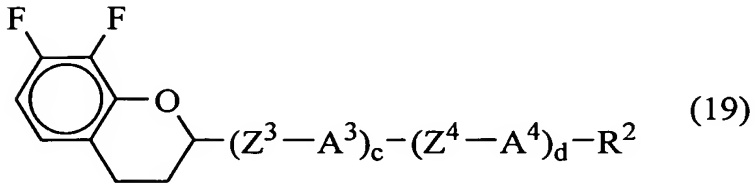
(wherein R^1, R^2, A^1, A^2, A^3, A^4, Z^1, Z^2, Z^3, Z^4, a, b, c, and d each independently represents the same meaning as that of general formula (1)). It is preferable that the reaction be carried out in the same system as that used for the reaction in which the alcoholate represented by the general formula (17) is produced.

[0045]

(Preparation Method 2)

By using 1,2,3-trifluorobenzene as a starting material in a similar manner to the reaction of Example 1, a chroman derivative represented by general formula (19)

[Chemical Formula 19]



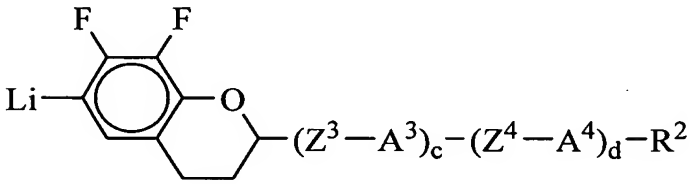
(19)

(wherein R^2, A^3, A^4, Z^3, Z^4, c, and d each independently represents the same meaning as that of general formula (1)) is produced.

The produced compound of general formula (19) is lithiated to produce a lithium compound represented by general formula (20)

[0046]

[Chemical Formula 20]



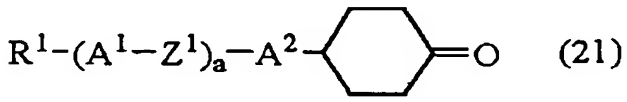
(20)

(wherein R^2, A^3, A^4, Z^3, Z^4, c, and d each independently represents the same meanings as that of general formula (1)).

[0047]

The produced compound represented by general formula (20) is reacted with a cyclohexanone derivative represented by general formula (21)

[Chemical Formula 21]

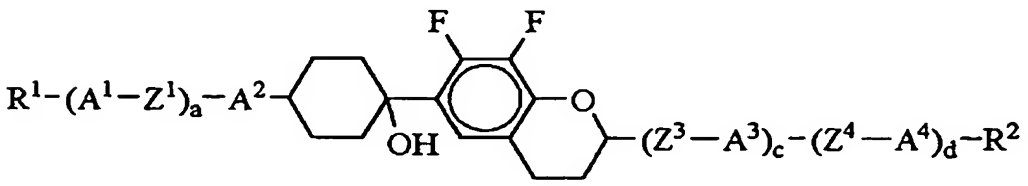


(21)

(wherein R^1, A^1, A^2, Z^1, and a each independently represents the same meaning as that of general formula (1)) to produce an alcohol represented by general formula (22)

[0048]

[Chemical Formula 22]



(22)

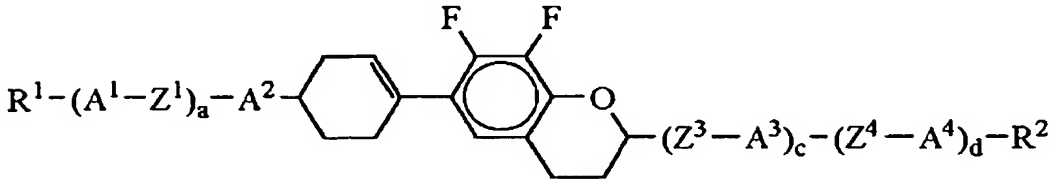
(wherein R^1, R^2, A^1, A^2, A^3, A^4, Z^1, Z^3, Z^4, a, c, and d each independently represents the same meaning as that of general formula (1)).

[0049]

The produced compound represented by general formula (22) is dehydrated to produce an olefin represented by general formula (23)

[0050]

[Chemical Formula 23]



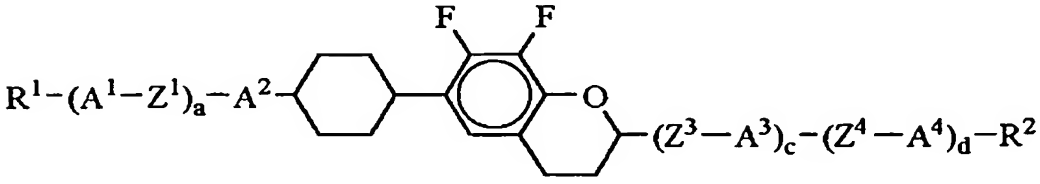
(23)

(wherein R^1, R^2, A^1, A^2, A^3, A^4, Z^1, Z^3, Z^4, a, c, and d each independently represents the same meaning as that of general formula (1)).

The produced compound represented by general formula (23) is hydrogenated to produce a chroman derivative represented by general formula (24)

[0051]

[Chemical Formula 24]



(24)

(wherein R^1, R^2, A^1, A^2, A^3, A^4, Z^1, Z^3, Z^4, a, c, and d each independently represents the same meaning as that of general formula (1)).

[0052]

[Examples]

Hereinafter, although the present invention will be further explained in reference to examples, the present invention is not limited to these examples. Moreover, "%" shown in compositions of the following examples and comparative examples indicates "% by mass".

[0053]

The following abbreviations are used for indicating compounds.

[0054]

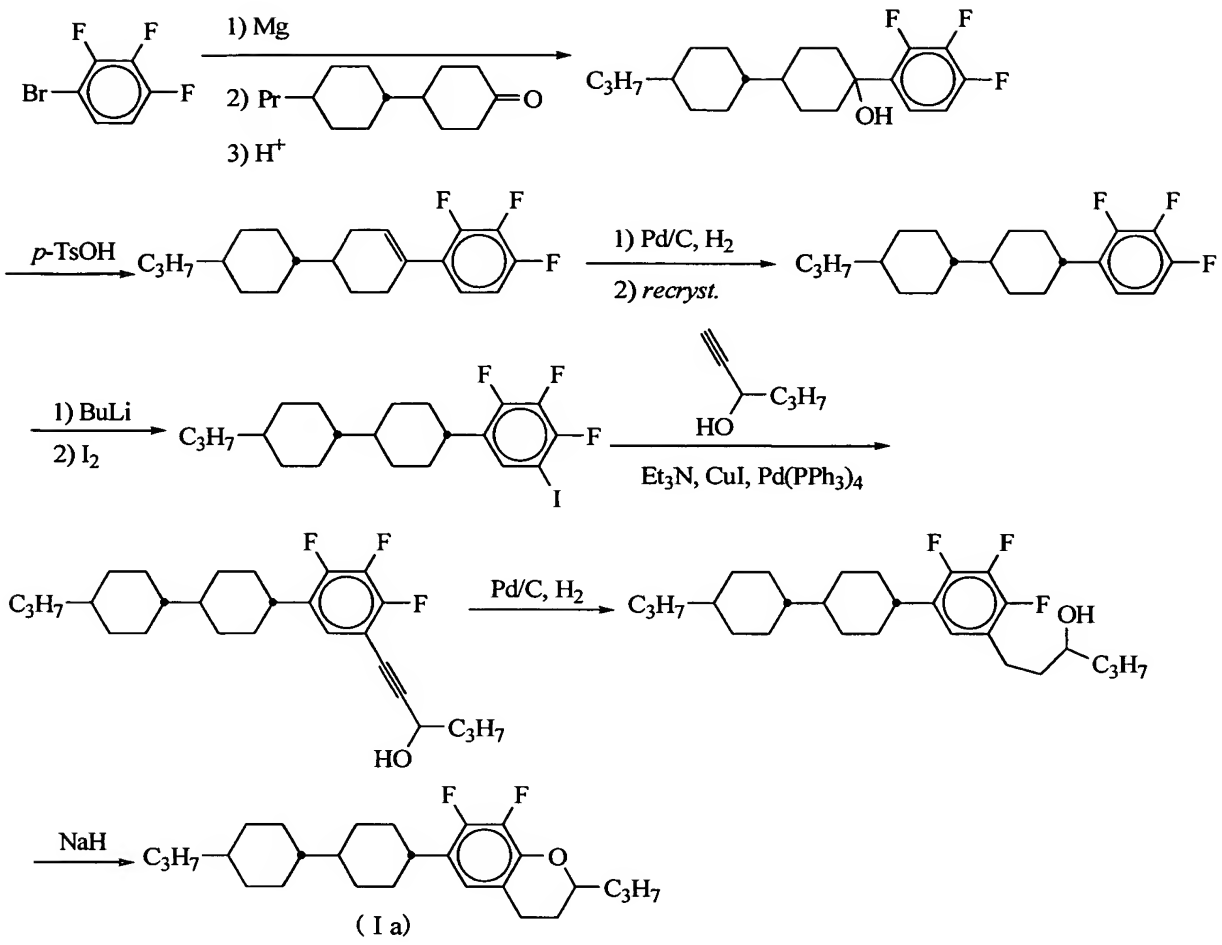
THF:	Tetrahydrofuran
DMF:	N, N-Dimethylformamide
p-TsOH:	*p*-Toluenesulfonate
Et:	Ethyl group
Bu:	Butyl group
CN:	Nitrile group

[0055]

(Example 1)

Synthesis of 7,8-difluoro-6-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-2-propylchroman (Ia)

[Chemical Formula 25]



[0056]

(1-1) Synthesis of 2,3,4-trifluoro-1-[1-hydroxy-4-(*trans-4*-propylcyclohexyl) cyclohexyl]benzene

7.6 g of magnesium and 20 mL of THF were stirred while water-cooling under a nitrogen atmosphere, a THF solution (200 mL) containing 60 g of 2,3,4-trifluorobromobenzene was added dropwise to the mixture for 2 hours, and then stirred for 3 hours. Into this, a THF solution (200 mL) containing 70 g of 4-(*trans*-4-propylcyclohexyl)cyclohexanone was added dropwise for 2 hours, and then stirred for 2 hours. After the reaction solution was poured into 10% hydrochloric acid and stirred for a while, an organic layer was separated, and an aqueous layer was

extracted with toluene. After the organic layer was mixed together, washed using water and a saturated saline solution in that order, and dried using anhydrous sodium sulfate, the solvent was evaporated under a reduced pressure to obtain 110 g of 2,3,4-trifluoro-1-[1-hydroxy-4-(*trans-4*-propylcyclohexyl)cyclohexyl]benzene (insufficiently dried).

MS *m/z* : 354 (M^+), 55 (100)

[0057]

(1-2) Synthesis of 2,3,4-trifluoro-1-[4-(*trans*-4-propylcyclohexyl) -1-cyclohexenyl]benzene

After 110 g of 2,3,4-trifluoro-1-[1-hydroxy-4-(*trans*-4-propylcyclohexyl) cyclohexyl]benzene (insufficiently dried) was dissolved into 400 mL of toluene, 10 g of *p*-toluenesulfonic anhydride was added to the mixture, and heated to reflux for 2 hours. After water was added and stirred for a while, an organic layer was separated, and an aqueous layer was extracted with toluene. After the organic layer was mixed together, washed using water and a saturated saline solution in that order, and dried using anhydrous magnesium sulfate, the solvent was evaporated under a reduced pressure. The residue was purified by column chromatography (silica gel, hexane) to obtain 93 g of 2,3,4-trifluoro-1-[4-(*trans*-4-propylcyclohexyl)-1-cyclohexenyl]benzene.

MS *m/z* : 336 (M^+), 69 (100)

[0058]

(1-3) Synthesis of 2,3,4-trifluoro-1-[*trans-4*-(*trans*-4-propylcyclohexyl) cyclohexyl]benzene

To 93 g of 2,3,4-trifluoro-1-[4-(*trans-4*-propylcyclohexyl)-1-cyclohexenyl] benzene which was dissolved into 300 mL of ethyl acetate, 9g of 5% palladium carbon

(50% in water) was added, and stirred for 5 hours at a hydrogen pressure of 0.5 MPa. After palladium carbon was removed by filtration, the solvent was evaporated under a reduced pressure to obtain 90 g of a mixture containing a light yellow oily material and a light yellow solid. 80 g of the mixture was purified by recrystallization (ethanol / methanol / hexane) to obtain 17 g of 2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene.

MS *m/z* : 338 (M^+), 69 (100)

[0059]

(1-4) Synthesis of 5-iodo-2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene

In a nitrogen atmosphere, 17 g of 2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene was dissolved into 300 mL of THF, and cooled to -60°C. Into this, 39 mL of butyllithium (1.56 M of hexane solution) was added dropwise for 30 minutes, and stirred for 2 hours. Into this, a THF solution (50 mL) containing 14 g of iodine was added dropwise for 1 hour, and warmed to room temperature. After the reaction solution was poured into a sodium thiosulfate aqueous solution, and stirred for a while, an organic layer was separated, and an aqueous layer was extracted with toluene. After the organic layer was mixed together, washed using water and a saturated saline solution in that order, and dried using anhydrous magnesium sulfate, the solvent was evaporated under a reduced pressure to obtain 25 g of 5-iodo-2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene.

MS *m/z* : 464 (M^+), 69 (100)

[0060]

(1-5) Synthesis of 5-(3-hydroxy-1-hexynyl)-2,3,4-trifluoro-1-[*trans*-4-(*trans*

-4-propylcyclohexyl)cyclohexyl]benzene

In a nitrogen atmosphere, 25 g of 5-iodo-2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene was dissolved into 300 mL of DMF, to which 21 mL of triethylamine, 0.19 g of copper iodide (I), and 0.58 g of tetrakistriphenylphosphine palladium (0) were added, followed by heating to 55°C. Into this, the DMF (30 mL) solution containing 5.9 g of 1-hexine-3-ol was added dropwise for 20 minutes, and stirred for 3 hours. After the reaction mixture was poured into a sodium thiosulfate aqueous solution, and stirred for a while, an organic layer was separated and an aqueous layer was extracted with toluene. After the organic layer was mixed together, washed using water, 10% hydrochloric acid twice, water, a saturated sodium hydrogen carbonate aqueous solution, and a saturated saline solution in that order, and dried using anhydrous magnesium sulfate, the solvent was evaporated under a reduced pressure. The residue was purified by sequentially carrying out column chromatography (silica gel, toluene) twice, activated carbon treatment (acetone), and column chromatography (silica gel, hexane / acetone), to obtain 20 g of 5-(3-hydroxy-1-hexynyl)-2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl) cyclohexyl]benzene.

MS *m/z* : 434 (M^+), 69 (100)

[0061]

(1-6) Synthesis of 5-(3-hydroxyhexyl)-2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene

To 20 g of 5-(3-hydroxy-1-hexynyl)-2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]benzene which was dissolved into 80 mL of ethanol, 2 g of 5% palladium carbon (50% in water) was added, stirred for 6 hours at a hydrogen

pressure of 0.5 MPa, and was then left to stand overnight. After palladium carbon was removed by filtration, the solvent was evaporated under a reduced pressure to obtain 10 g of 5-(3-hydroxy-1-hexyl)-2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl) cyclohexyl]benzene.

MS *m/z* : 438 (M^+), 420 (100)

[0062]

(1-7) Synthesis of 7,8-difluoro-6-[*trans*-4-(*trans*-4-propylcyclohexyl) cyclohexyl]-2-propylchroman

Under nitrogen replacement, 1.23 g of sodium hydride (60% in oil) was suspended in 18 ml of DMF. Into this, the THF (36 mL) solution containing 9 g of 5-(3-hydroxyhexyl)-2,3,4-trifluoro-1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl] benzene was added dropwise for 30 minutes, and stirred for 3 hours at 40°C and then for 3 hours at 50°C. After toluene was added and stirred for a while, an organic layer was separated and an aqueous layer was extracted with toluene. After the organic layer was mixed, washed using water and a saturated saline solution in that order, and dried using anhydrous sodium sulfate, the solvent was evaporated under a reduced pressure. The residue was purified by carrying out column chromatography (silica gel, hexane), recrystallization (hexane), recrystallization (hexane / ethanol) to obtain 2.5 g of 7,8-difluoro-6-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-2-propylchroman as colorless needlelike crystals.

MS *m/z* : 418 (M^+, 100)

^{1}H-NMR (400 MHz, $CDCl_3$)

δ(ppm): 0.87 (t, J = 7.6 Hz, 3 H), 0.97 (t, J = 7.2 Hz, 3 H), 1.1 – 1.2 (m, 6 H), 1.25 – 1.65 (m, 10 H), 1.65 – 1.9 (m, 12 H), 1.95 – 2.05 (m, 1 H), 2.6 – 2.85 (m, 3 H), 3.9 – 4.05 (m,

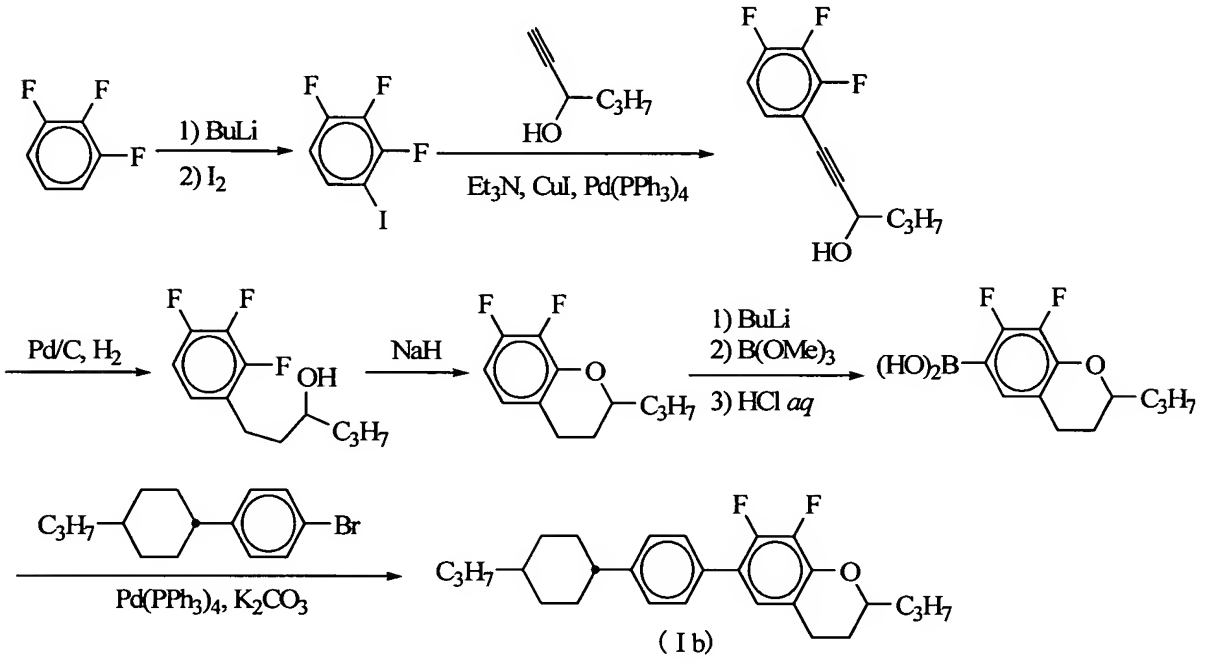
1H), 6.58 (d, J = 6.4 Hz, 1 H)

[0063]

(Example 2)

Synthesis of 6-[4-(*trans*-4-propylcyclohexyl)phenyl]-7,8-difluoro-2-propylchroman (Ib)

[Chemical Formula 26]



(Ib)

[0064]

(2-1) Synthesis of 4-iodo-1,2,3-trifluorobenzene

In a nitrogen atmosphere, 1,2,3-trifluorobenzene was dissolved into THF, and cooled to -60°C. Then, butyllithium (1.56 M hexane solution) was added dropwise for 30 minutes, and stirred for 2 hours. Then, the THF solution containing iodine was added dropwise for 1 hour, and warmed to room temperature. After the reaction solution was poured into a sodium thiosulfate aqueous solution and stirred for a while, an organic layer was separated, and an aqueous layer was extracted with toluene. After the organic layer was mixed, washed using water and a saturated saline solution in that order,

and dried using anhydrous magnesium sulfate, the solvent was evaporated under a reduced pressure to obtain 4-iodo-1,2,3-trifluorobenzene.

[0065]

(2-2) Synthesis of 1-(3-hydroxy-1-hexynyl)-2,3,4-trifluorobenzene

In a nitrogen atmosphere, 4-iodo-1,2,3-trifluorobenzene was dissolved into DMF, into which triethylamine, copper iodide (I), and tetrakistriphenylphosphine palladium (0) were added and heated to 55°C. Then, the DMF solution containing 1-hexine-3-ol was added dropwise for 20 minutes, and stirred for 3 hours. After the reaction mixture was poured into a sodium thiosulfate aqueous solution, and stirred for a while, an organic layer was separated, and an aqueous layer was extracted with toluene. After the organic layer was mixed, washed using water, 10% hydrochloric acid twice, water, a saturated sodium hydrogen carbonate aqueous solution, and a saturated saline solution in that order, and dried using anhydrous magnesium sulfate, the solvent was evaporated under a reduced pressure. The residue was purified by column chromatography (silica gel, toluene / hexane) to obtain 1-(3-hydroxy-1-hexynyl)-2,3,4-trifluorobenzene.

[0066]

(2-3) Synthesis of 1-(3-hydroxyhexyl)-2,3,4-trifluorobenzene

After 1-(3-hydroxy-1-hexynyl)-2,3,4-trifluorobenzene was dissolved in ethanol, 5% palladium carbon (50% in water) was added thereto, and stirred for 6 hours at a hydrogen pressure of 0.5 MPa, and the mixture was left to stand overnight. After palladium carbon was removed by filtration, the solvent was evaporated under a reduced pressure to obtain 1-(3-hydroxyhexyl)-2,3,4-trifluorobenzene.

[0067]

(2-4) Synthesis of 7,8-difluoro-2-propylchroman

Sodium hydride (60% in oil) was suspended in DMF under nitrogen replacement. Then, the THF solution containing 1-(3-hydroxyhexyl)-2,3,4-trifluorobenzene was added dropwise for 30 minutes, and stirred for 3 hours at 50°C. After toluene was added and stirred for a while, an organic layer was separated and an aqueous layer was extracted with toluene. After the organic layer was mixed, washed using water and a saturated saline solution in that order, and dried using anhydrous sodium sulfate, the solvent was evaporated under a reduced pressure. The residue was purified by column chromatography (silica gel, hexane) to obtain 7,8-difluoro-2-propylchroman.

[0068]

(2-5) Synthesis of 7,8-difluoro-2-propylchroman-6-borate

In a nitrogen atmosphere, 7,8-difluoro-2-propylchroman was dissolved in THF, and was then cooled to -60°C. Then, butyllithium (1.56 M hexane solution) was added dropwise for 30 minutes, and the mixture was then stirred for 2 hours. Then, the THF solution of trimethyl borate was added dropwise for 1 hour, and warmed to room temperature. After the reaction solution was poured into 10% hydrochloric acid, and stirred for 2 hours, an organic layer was separated, and an aqueous layer was extracted with toluene. After the organic layer was mixed, washed using water and a saturated saline solution in that order, and dried using anhydrous magnesium sulfate, the solvent was evaporated under a reduced pressure to obtain 7,8-difluoro-2-propylchroman-6-borate.

[0069]

(2-6) Synthesis of 6-[4-(*trans*-4-propylcyclohexyl)phenyl]-7,8-difluoro-2-propylchroman

In a nitrogen atmosphere, 4-(*trans*-4-propylcyclohexyl)bromobenzene was

dissolved in toluene, to which 7,8-difluoro-2-propylchroman-6-borate, potassium carbonate, water, and tetrakistriphenylphosphine palladium (0) were added. The mixture was stirred for 5 hours at 90°C under pressure. After the reaction mixture was poured into water and stirred for a while, an organic layer was separated and an aqueous layer was extracted with toluene. After the organic layer was mixed, washed using water, 10% hydrochloric acid, and a saturated saline solution in that order, and dried using anhydrous magnesium sulfate, the solvent was evaporated under a reduced pressure. The residue was purified by carrying out column chromatography (silica gel, toluene) and recrystallization (toluene / hexane) to obtain 6-[4-(*trans*-4-propylcyclohexyl)phenyl] -7,8-difluoro-2-propylchroman.

^{1}H-NMR (400 MHz, $CDCl_3$)

δ(ppm): 0.92 (t, J = 7.2 Hz, 3 H), 0.97 (t, J = 7.2 Hz, 3 H), 1.1 – 1.5 (m, 11 H), 1.5 – 2.1 (m, 8 H), 2.5 – 2.9 (m, 3 H), 3.9 – 4.1 (m, 1H), 6.6 – 7.0 (m, 1 H), 7.1 – 7.6 (m, 4 H)

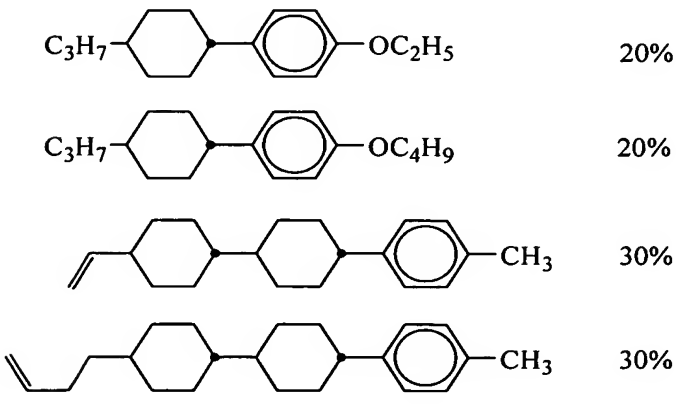
[0070]

(Example 3)

Preparation of liquid crystal composition (1)

A host liquid crystal composition (H) having the following components:

[Chemical Formula 27]



(H)

[0071]

was prepared. The physical values of the composition (H) are as follows.

Nematic Phase Upper Limit Temperature (T_{N-I}) : 103.2°C

Dielectric Anisotropy ($\Delta\varepsilon$) : 0.03

Refractive Index Anisotropy (Δn) : 0.099

A liquid crystal composition (M-1) containing 90% of this host liquid crystal (H) and 10% of the compound (Ia) prepared in Example 1 was prepared. The physical values of this composition are as follows.

[0072]

Nematic Phase Upper Limit Temperature (T_{N-I}) : 109.0°C

Dielectric Anisotropy ($\Delta\varepsilon$) : -0.52

Refractive Index Anisotropy (Δn) : 0.098

In comparison with the host liquid crystal composition (H), the liquid crystal composition (M-1) containing the compound (Ia) according to the present invention had an increased nematic phase upper limit temperature (T_{N-I}) and a dielectric anisotropy ($\Delta\varepsilon$) which decreased to a negative value. Thus, it was shown that the compound represented by formula (Ia) according to the present invention stably exhibited a nematic phase even at high temperature, and had a negative dielectric anisotropy of which the absolute value was extremely large.

[0073]

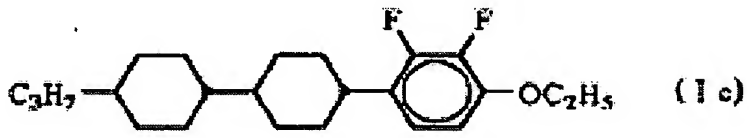
(Comparative Example 1)

Preparation of liquid crystal composition (2)

A liquid crystal composition (M-2) containing 90% of the host liquid crystal (H) prepared in Example 3 and 10% of a compound disclosed in Patent Document 1, the

compound being represented by formula (Ic):

[Chemical Formula 28]



(Ic)

was prepared. The physical values of the composition are as follow.

[0074]

Nematic Phase Upper Limit Temperature (T_{N-I}) : 110.2°C

Dielectric Anisotropy ($\Delta\varepsilon$) : -0.48

Refractive Index Anisotropy (Δn) : 0.100

It was apparent that the liquid crystal composition (M-2) containing the compound represented by formula (Ic) disclosed in Patent Document 1 has approximately the same nematic phase upper limit temperature (T_{N-I}), but a smaller absolute value of dielectric anisotropy, in comparison with the composition (M-1) described in Example 1.

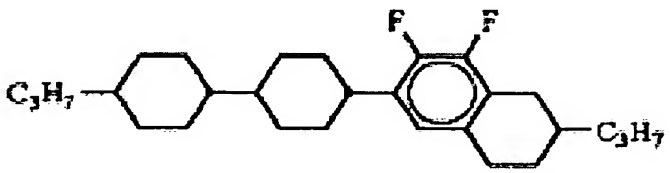
[0075]

(Comparative Example 2)

Preparation of liquid crystal composition (3)

A liquid crystal composition (M-3) containing 90% of the host liquid crystal composition (H) prepared in Example 3 and 10% of a compound disclosed in Patent Document 2, the compound being represented by formula (Id)

[Chemical Formula 29]



(Id)

was prepared. The physical values of this composition are as follows.

[0076]

Nematic Phase Upper Limit Temperature (T_{N-I}) : 109.4°C

Dielectric Anisotropy ($\Delta\varepsilon$) : -0.22

Refractive Index Anisotropy (Δn) : 0.099

It was apparent that the liquid crystal composition (M-3) containing the compound represented by formula (Id) described in Patent Document 2 has approximately the same nematic phase upper limit temperature (TN-1), but a smaller absolute value of dielectric anisotropy, in comparison with the composition (M-1) described in Example 1.

[0077]

[Effects of the Invention]

The chroman derivative of the present invention has characteristics in that the dielectric anisotropy is negative and the absolute value thereof is large. The liquid crystal composition and the liquid crystal display element, which include the compound as their constituent, are useful as liquid crystal display elements of a vertical alignment mode, IPS mode, or the like.

[Document Type] Abstract

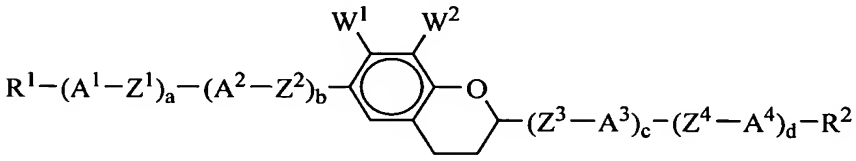
[Abstract]

[Problem to be Solved by the Invention] To provide a liquid crystal compound having a large absolute value of negative dielectric anisotropy and to provide a liquid crystal composition useful for various display systems using a liquid crystal compound having a negative dielectric anisotropy such as vertical alignment mode, IPS or the like.

[Means for Solving the Problem]

The present invention provides a chroman derivative represented by general formula (1)

[Chemical Formula 1]



(1)

and a liquid crystal composition using the same, and further provides a liquid crystal display element using the same. Using the compound of the present invention, a liquid crystal composition with a negative dielectric anisotropy suitable for vertical alignment mode, IPS or the like can be obtained.

[Selected Drawing] None